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Attached is the English language translation of Nishihama WO 02/24153 as requested by Applicant.

  
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METAL OXIDE/SILICA COMPOSITE AND COSMETIC COMPRISING THE SAME  
[KINZOKU SANKA BUTSU/SIRIKA FUKUGO TAI NARABI NI SORE O GANMU  
KESHO RYO]

SHUJI NISHIHAMA

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Abstract:

The purpose of the invention is to offer a cosmetic comprising the metal oxide, the metal oxide exhibits enhanced dispersion of the metal oxide and thus can be used for preparing a UV ray protecting powder and cosmetic which have satisfactory UV ray protecting capability and transparency.

A metal oxide/silica composite which comprises a finely dispersed system comprising metal oxide particles having a primary particle diameter of 1 to 1000 nm and silica particles which are both dispersed in each other substantially in the state of the primary particles; and a metal oxide/silica composite, characterized in that it is prepared by admixing (1) a dispersion containing a silica sol having a primary particle diameter of 1 to 150 nm and (2) a particular metal oxide or metal oxide sol having a primary particle diameter of 1 to 1000 nm. In particular, the metal oxide/silica composite, wherein the particulate metal oxide or metal oxide sol comprises 1 or 2 or more of

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<sup>1</sup> the numbers in the margin indicate pagination in foreign text

titanium oxide, zinc oxide and cerium oxide. A cosmetic comprising the above metal oxide/silica composite. The metal oxide/silica composite exhibits enhanced dispersion of the metal oxide and thus can be used for preparing an UV ray protecting powder and cosmetic which have satisfactory UV ray protecting capability and transparency. /1

### Specification

Cosmetic comprising metal oxide/silica composite

This application has a priority claim number of Japan Patent Application number 2000 - 29084, filed on September 25, 2000.

[Technology field]

The invention pertains to the cosmetic comprising the metal oxide/silica composite. In particular, it pertains to the improvement of the dispersion capability of the metal oxide.

[Background technology]

The UV ray protecting powder such as titanium oxide and zinc oxide has a demerit in that the finish does not look natural and becomes white during application but on the other hand, it has a merit due to its excellence in safety as compared to the UV ray absorbent that is typically represented by octyl methoxy cinnamate. In contrast to this, if the titanium oxide is coated with the

transparent powder such as silica, it is known to improve the transparency of the powder. Also, when ultra fine particle powder such as zinc oxide and sol solution are combined in the cosmetic, the transparency is improved as compared to the type when combined conventionally with the zinc oxide and titanium oxide.

However, if the titanium oxide is coated with the transparency powder such as silica, the proportion in the coating is increased, the tendency that was observed is that the UV ray protecting capability is reduced. Also, when the ultra fine particle powder such as titanium oxide and zinc oxide and the sol solution are combined in the cosmetic, over time, the powder or sol is deposited and coagulated. As a result, this affects the stability and reduced the UV ray protecting capability.

[Disclosure of the invention]

The purpose of the invention is to offer a metal oxide with high dispersion capability so a cosmetic and UV ray protecting powder can be offered with sufficient transparency and UV ray protecting capability.

The inventors mixed directly the silica sol and the sol solution or the fine particle dispersion body consisting of a metal oxide having UV ray protecting capability, for example, titanium oxide, zinc oxide and

selenium oxide, both of these are coagulated and a gel is obtained. In addition, the inventors mixed the silica sol dispersion body and the sol solution or the fine particle dispersion body having a pH that will not coagulate mutually, then, the metal oxide and the silica sol are coagulated simultaneously using acid or alkaline, by adjusting the pH till it precipitates, the powder composite of these is obtained. Then, the inventors discovered that when the metal oxide having a primary particle size and the silica particles of these powders are dispersed in the fine particle size, the structure of these powders obtained have high transparency and UV ray protecting capability. Also, when the inventors combined the sun screen with this composite powder, they discovered that not only it has high UV ray protecting capability, a natural finish can be provided without a whitening effect during application of the powder, thus, the invention attained success. /2

That is, the metal oxide/silica composite of the invention is characterized as a finely dispersed system comprising metal oxide particles having a primary particle diameter of 1 to 1000 nm.

Also, in the metal oxide/ silica composite of the invention, (1) the dispersion body containing a silica sol of primary particle size of 1 - 150 nm and (2) a particular



metal oxide or metal oxide sol having a primary particle diameter of 1 to 1000 nm.

Also, in the metal oxide/silica composite of the invention, after mixing the aforementioned dispersion body and the metal oxide of fine particles or the metal oxide sol, the pH of the solution is changed, the silica and metal oxide are coagulated and precipitated simultaneously.

Also, the metal oxide/silica composite of the invention, wherein the particulate metal oxide or metal oxide sol comprises one or more of titanium oxide, zinc oxide and cerium oxide, 1 or 2 or more of these can be combined.

Also, the metal oxide/silica composite of the invention is characterized as the metal oxide/silica composite of gel composition.

Also, the metal oxide/silica composite of the invention is characterized as the powder composition obtained by drying the aforementioned gel composition.

Also, it is preferred that the composite amount of the metal oxide is 5 - 90 wt. % to the total composite in the metal oxide/silica composite of the invention.

Also, the cosmetic of the invention is characterized as combining the aforementioned metal oxide/silica composite.

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[Brief explanation of the diagrams]

Figure 1 is the diagram showing the transparency of the comparison example 1 and the titanium oxide/silica composite (Implementation example 1).

Figure 2 is the diagram showing the transparency of the titanium oxide/silica composite (Implementation examples 1 - 2 and 1 - 3).

Figure 3 is the diagram showing the X ray diffraction pattern of the titanium oxide/silica composite (Implementation example 1 -2).

Figure 4 is the scanning electronic microscope photograph of the titanium oxide/silica composite.

Figure 5 is the TEM photograph of the titanium oxide/silica composite.

[The optimum state for implementing the invention]

The detail content of the invention is explained below.

The silica sol of the invention is the fine colloidal silica dispersed uniformly in the solution. A commercial product is the "Snodex" silizoo made by Hisan Chemical Plant. The dispersion medium used at this time is water, isopropanol, methyl ethyl ketone, one that does not affect the dispersion stability of the silica sol particle. Also, when the dispersion medium is an aqueous solution, the

silica sol solution is selected based on the acidity or basic property and it match the equal electric point of the metal oxide sol or the metal oxide fine particles that are combined. The production of the metal oxide/silica particles can be controlled, the composite particles of high dispersion capability and of uniform dispersion are preferred.

The particle size of the silica sol used in the invention is 1 - 150 nm, preferably 5 - 100 nm. When the particle size is too large or conversely, it is too small, the silica sol cannot enter between the titanium sol particle and the titanium sol cannot be dispersed uniformly. The silica particle and the titanium oxide are produced into coagulated pieces as a result of this. The UV ray protecting capability is reduced and the whitening appearance is produced.

The fine particle metal oxide or the metal oxide sol of the invention is the metal oxide or sol particle selected from 1 type or 2 or more types of these, titanium oxide, zinc oxide and selenium oxide. The metal oxide or sol particles can be selected from the solid body of 2 or more of these, titanium oxide, zinc oxide and selenium oxide, also, the solids of other metal oxide can be used. The primary particle size is 1 - 1000 nm but preferably 5 -

500 nm. If the particle size is above this prescribed range, the composite effect of the silica sol cannot be realized. Conversely, the part that is combined with the silica, the UV ray protecting capability is reduced. Also, the material having high UV ray protecting capability cannot be obtained with the composite powder having the particle size of these metal oxide or sol. /4

An example of the pH adjusting agent for making into gel the composite body, an alkaline agent or acid is generally used. The examples of the acid used are such as hydrochloric acid, acetic acid, citric acid, sulfuric acid, phosphoric acid and nitric acid. An example of the alkaline agent used is sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate and ammonia water.

The combined amount of the metal oxide in the metal oxide/silica complex of the invention is 5 - 90 wt.% but preferably 25 - 80 wt. % of the total amount. When the combined amount is below this range, the material containing this UV ray protecting capability which is the purpose of the invention cannot be obtained. When the combination is above this range, the metal oxide or the sol particle becomes coagulated, the material obtained has a reduced UV ray protecting capability.

The drying temperature of the composite is from room temperature - 200 deg C but preferably 80 - 120 degree C. The silica sol condensate is produced after drying the composite. Since the titanium sol particles can be dispersed and maintained in a stable manner, the composite that is formed has a shape where the silica sol cannot keep its initial shape.

When the metal oxide or silica sol is compounded, the metal oxide or sol can be combined and compounded simultaneously. For example, the metal oxide or the sol particles can be compounded, the metal oxide or the sol particle examples such as aluminum oxide (alumina), iron oxide, copper oxide, magnesium oxide, nickel oxide, zirconium oxide can be compounded. Also, the metal particles to be compounded are the metal colloidal particles.

The following can be used for the hydrophobic treatment of the of the metal oxide/silica complex obtained in the invention, the aliphatic acid silica such as aluminum stearate, zinc myristate; the aliphatic acid such as stearic acid, palmitic acid; wax such as candiriraro and cannavaro; the modified silicon such as the polyoxy ethylene modified silicon; the carboxy modified silicon and the amino modified silicon; the silicon oil such as methyl

polysiloxane, methyl phenyl polysiloxane or the dextrin aliphatic ester can be used.

Other additives can be used in the cosmetic of the invention like the ones used in a normal cosmetic, the usage amount is at a range that will not damage the effect of the invention. /5

For example, Vaseline, lanolin, ceresin, cannavaro, candiriraro, the solid high grade alcohol, the semi-solid oil, squalane, fluid paraffin, fluid oil such as ester oil, the oil such as silicone oil, sodium hyaluronic acid, the humidity protectant such as glycerin, the surface active agents such as the cation type surface active agent and the non-ionic surface active agent, the dye, the rust proofing agent, fragrance and anti-oxidant.

The invention is explained in further detail below according to the implementation examples and the comparison examples but the range of the invention is not limited to these implementation examples. The inventors made the powder having the UV ray protecting capability for the Implementation examples and the comparison examples given below. Silica sol is used in the Implementation examples and the silica sol is not used in the comparison examples.

<Implementation example 1-1>

50 g of Snodex O (silica sol made by Hisan Chemical, silica content of 20%, primary particle size is 10 - 20 nm) and 100 g of TSK - 5 (titania sol made by Isinara Chemicals, rutile type, titanium oxide content of 30%, the primary particle size of 10 - 100 nm) are mixed. 0.1 M sodium hydroxide solution is dropped into a dispersed solution until it becomes uniform. The pH is adjusted = 9, a gel substance is obtained. This is filtered, this is washed repeatedly with water for 5 times and the solid substance is dried at 100 - 110 deg. C, the titanium oxide/silica composite powder is obtained that is dispersed in water.

<Implementation example 1-2>

15 g of Snodex O (silica sol made by Hisan Chemical, silica content of 20%, primary particle size is 10 - 20 nm) and 268 ml of titania sol aqueous solution (pH = 1, 8g content as the anatase type  $\text{TiO}_2$ , the primary particle size of 10 - 100 nm) are mixed. 0.1 M sodium hydroxide solution is dropped into a dispersed solution until it becomes uniform. The pH is adjusted = 8.5, a gel substance is obtained. This is filtered, this is washed repeatedly with water for 5 times and the solid substance is dried at 90

deg. C, the titanium oxide/silica composite powder is obtained that is dispersed in water.

<Implementation example 1-3>

40 g of Snodex O (silica sol made by Hisan Chemical, silica content of 20%, primary particle size is 10 - 20 nm) and 268 ml of titania sol aqueous solution (pH = 1, 8g content as the anatase type  $\text{TiO}_2$ , the primary particle size of 10 - 100 nm) are mixed. 0.1 M sodium hydroxide solution is dropped into a dispersed solution until it becomes uniform. The pH is adjusted = 8.5, a gel substance is obtained. This is filtered, this is washed repeatedly with water for 5 times and the solid substance is dried at 90 deg. C, the titanium oxide/silica composite powder is obtained that is dispersed in water. /6

<Implementation example 2>

100 g of Snodex 30 (silica sol made by Hisan Chemical, silica content of 30%, primary particle size is 10 - 20 nm) and 100 g of TSK -5 are mixed. 0.5 M of diluted hydrochloric acid is dropped into the dispersed solution. The pH is adjusted to 7 - 8. The gel obtained is filtered, this is washed repeatedly with water for 5 times and the solid substance is dried at 100 - 110 deg. C, the titanium oxide/silica composite powder is obtained that is dispersed in water.



<Implementation example 3>

The zinc oxide powder (primary particle size of 50 - 100 nm) described in the Implementation example of the WO99/25654 in the Snodex XL (silica sol made by Hisan Chemicals, silica content of 40%, the primary particle size of 40 - 60 nm) is dispersed to a proportion of silica sol : zinc oxide = 25:75. 0.1 M of hydrochloric acid is dropped into the dispersed solution. This is dried and pulverized into a gel form. This powder is washed with water and dried. The zinc oxide/silica composite powder is obtained.

<Implementation example 4>

Silica sol/isopropyl alcohol dispersion body (IPA - ST, silica content of 30%, the primary particle size of 10 - 20 nm) and cerium oxide sol (the primary particle size of 50 - 100 nm) are mixed to a proportion of silica sol: cerium oxide = 35:65. The obtained dispersion body is agitated using a kneader and then dried, cerium oxide/silica composite powder is obtained.

<Implementation example 5>

15 g of Snodex O (silica sol made by Hisan Chemical) and 30 g of alumina sol 100 (alumina content of 10 - 11% are mixed. This mixture is mixed with 100 g of titania sol (TSK - 5). 0.2 M of sodium hydroxide solution is dropped into the dispersed solution until uniform. The pH is

adjusted = 7. The gel obtained is filtered, this is washed repeatedly with water for 5 times and the solid substance is dried at 100 - 110 deg. C, the titanium oxide/silica composite powder is obtained that is dispersed in water.

<Comparison example 1>

Fine titanium oxide particles (Titanium oxide 100AL made by Teika, the primary particle size of about 30 nm) and aerodil #200 (silica gel made by Japan Aerodil, the primary particle size of 12 nm) are mixed to a ratio of 3 : 1, a mixture is prepared after agitating for 1 minute with an air midi. This becomes comparison example 1. /7

<Comparison example 2>

30 g of water glass is dissolved in 150 g of water, titanium sol TSK-5 of 100 g is added to the aforementioned aqueous solution. This solution is adjusted to a pH of 7 - 8 using 0.5 M of dilute hydrochloric acid, then it is heated and dried with a kneader. The powder that is obtained is washed with water and then dried and pulverized, this is used as comparison example 2.

<Comparison example 3>

20 g of sodium meta silicic acid is dissolved in 300 g of water, the zinc oxide powder as described in the implementation example of the W099/25654 is dispersed in this solution. This solution is adjusted to a pH = 8 using

1 M of dilute hydrochloric acid, then, the dispersion is filtered and dried, this is used as comparison example 3.

<Comparison example 4>

The cerium oxide sol and the ortho silicic acid tetra ethyl is mixed to a proportion of cerium oxide:silica portion of 65:35, this is hydrolyzed for 12 hours at 80 deg C. The reactant that is obtained is filtered, washed, then, dried and pulverized. This is used as comparison example 4.

The inventors conduct the following comparison tests using the aforementioned powder.

Comparison tests 1 - 1

The inventors compare the powder from comparison example 1 which is the mixture of silica particles and the titanium oxide particle and the powder from Implementation example 1-1 which is the titanium/silica composite of the invention.

The respective powder obtained from the implementation example 1-1 and the comparison example 1 are mixed into the castor oil to a proportion of 1:9 to castor oil. A slurry containing each of the powder and the castor oil is obtained. Each slurry is mixed with a three rollers. After the mixing, the slurry is coated onto a quartz plate with a 5 micrometer applicator. The UV ray permeability of that

coated film is measured with a photometer (U-3410 made by Hitachi Manufacturing Plant).

Figure 1 is the measurement result of the slurry that is obtained with the comparison experiment 1. From the result of figure 1, in implementation example 1 - 1, the UV ray permeability to the UVB of 290 - 329 nm is the same as the comparison example 1. By compounding with the titanium oxide and the silica particles, pertaining to the visible range, the permeability is higher as compared to the comparison example 1. The transparency is high while having the same UV ray protecting capability. An excellent effect can be obtained. /8

Similar to the comparison experiment 1, the powder of Implementation example 1 - 3 and Implementation example 1 - 2 which are the titanium oxide/silica composite produced from the titanium oxide and silica sol and the castor oil is made into a slurry, this is formed into a coated film, the UV ray permeability of that coated film is measured with photometer (U-3410 made by Hitachi Manufacturing).

The result is shown in figure 2. Similar to Implementation example 1 - 1, by compounding the titanium oxide and silica particles, the powder has excellent transparency and the UV ray protecting capability for

Implementation examples 1 - 2 and Implementation examples 1 - 3.

The X ray diffraction pattern of the composite

Next is the analysis of the metal oxide/silica composite by the inventors according to the X ray diffraction pattern. Figure 3 is the X ray diffraction pattern of the titanium oxide/silica composite of the Implementation examples 1 - 2. According to the result of figure 3, there is no peak beside the main peak of titanium oxide. This shows the dispersion of the titanium oxide in the titanium oxide/silica composite in the primary particle state.

The composite amount of the metal oxide

The inventors research the composite content of the metal oxide, the titanium oxide/silica composite is produced having the composition shown in Table 1 given below. According to the comparison experiment 1, the permeability of the composite at 310 nm is measured, the UV ray protecting effect is evaluated according to the evaluation standard shown below.

(Evaluation standards: UV ray protecting effect)

O permeability at 310 nm is below 10 %

0 permeability at 310 nm is above 10 % but below 20 %

A permeability at 310 nm is above 20 % but below 30 %

x permeability at 310 nm is above 30 %

Table 1

Titanium oxide amount      silica amount      UV ray effect

(wt. %)

(wt. %)

1

99

x

5

95

○

10

90

△

30

70

○

50

50

⊙

75

25

⊙

85

15

○

90

10

○

95

5

△

/9

From the result of Table 1, the composite amount of the metal oxide in the metal oxide/silica composite is 0 wt. % shown in Table 2 of the result 5 - 9 but preferably at 25 - 80 wt. %.

Next, the inventor investigate the relationship of the half value width in  $d = 3.25$  (the rutile type titanium oxide of  $(hkl) = (110)$  surface is the peak) and the

titanium oxide concentration in the titanium oxide/silica composite.

Table 2

Titanium oxide Concentration	Half value width (100% of titanium oxide becomes 1) at $d = 3.25$
---------------------------------	--

17%	1.40
60%	1.22
88%	1.11
<u>100%</u>	<u>1.00</u>

According to the result of Table 2, the half value width is large as the titanium oxide amount is less. The crystallinity of the titanium oxide is poor. The titanium oxide in the composite is dispersed uniformly with the primary particle.

The scanning electronic microscope photo is shown in figure 4 for the titanium oxide/silica composite (Implementation example 1 - 2) of the invention. The titanium oxide and silica in the primary particles form can be realized from figure 4, these can be dispersed uniformly.

The specific surface area of the composite

Next is the investigation of the specific surface area of the titanium oxide/silica composite by the inventors. The result is shown in Table 3. (1) and (2) is the raw

material. (3) is the measurement value for the composite.

(4) is the proposed value for the computation of the

composite.

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Table 3

Specific surface area (m<sup>2</sup>/g)

(1)	Dry titania sol	265.7
(2)	Silica sol	239.8
(3)	Titanium oxide/silica composite (titanium oxide: silica = 70:30)	
		291.3
(4)	The titanium oxide/silica composite computed from (1) and (2)	257.9

From the result of Table 3, the specific surface area of the titanium oxide/silica composite of the real measurement value is larger than the titanium oxide/silica composite computed from the titania sol and silica sol which are the raw material. Therefore, by forming the composite, it is difficult for the coagulation in the particle.

#### Comparison experiment 2

The inventor made a sunscreen of the O/W emulsion type using the powder obtained with the Implementation example 2 and comparison example 2. Then, in the cosmetic, the comparison is performed for the cosmetic using the powder of implementation example 2 of the invention that is



compounded with the titanium oxide and silica sol and the cosmetic that used the powder of comparison example 2 that is compounded not using the silica sol. The preparing method is shown below according to Table 4.

Table 4

Implementation example 6                      O/W emulsion type sun screen

1. The powder obtained from Implementation example 2

2. Zinc powder

3. stearic acid

4. cetyl alcohol

5. Vaseline /11

6. silicone oil

7. fluid paraffin

8. Glyceryl monostearic acid ester (self emulsion type)

9. polyoxy ethylene (25 mole) mono-olate acid ester

10. polyethylene glycol 1500

11. bee gum

12. purified water

13. fragrance suitable amount

14. Rust proofing agent suitable amount

[Preparation method]

After 10 is added to 12, it is heated and dissolved, 11 is added, it is maintained at 70 deg. C and dispersed uniformly with a homogenous mixer. This becomes the water

phase. 3 - 9 and 13 and 14 are mixed. This is kept at 70 deg C, heated and dissolved. This becomes the oil phase. Powder 1 and 2 are added to the water phase and dispersed with a homogenous mixer. An oil phase is added to this, this mixture is emulsified and dispersed uniformly in a homogenous mixer. After emulsifying, it is cooled to 35 deg C while being mixed. A sun screen of Implementation example 6 is obtained as described above.

In the O/W emulsion type sun screen of implementation example 6, the powder obtained with comparison example 2 is combined instead of the powder obtained with Implementation example 2, this is used as comparison example 5. The product of implementation example 6 and the product of comparison example 5 are coated on the skin, directly after coating, the appearance of white is judged by the naked eye. The evaluation standard is given below. The results are shown in Table 5.

(The evaluation standard: the transparency)

O there is transparency

A some whitening has appeared, the transparency is less

X there is whiteness, there is no transparency

Table 5

Implementation example 6    Comparison example 5

Transparency                      0                                      A                                      /12

According to the result of Table 5, the implementation example 6 that contained the composite that is finely dispersed with the silica particles of the primary particles and the fine particle titanium oxide of Implementation example 2 are sun screens having good finish and not whiteness right after application. In contrast to this, for the comparison example 5 containing the powder of comparison example 2, the fine dispersion of the titanium oxide is insufficient so there is white appearance during the sunscreen application. Also, comparison example 5 is difficult to have a uniform coating. Therefore, during the production of the composite, the titanium oxide cannot be dispersed well like the one used in the invention since silica sol is not used.

Comparison experiment 3

The inventors made an oil base stick foundation using the powder obtained from Implementation example 3 and comparison example 3. Then, the comparison is performed for the cosmetic that used the powder of implementation example 3 of the invention that is compounded with the silica sol and the fine particles of zinc oxide powder and the cosmetic using the powder of comparison example 3

compounded using the silica sol. Both of these are shown in Table 6, the testing method is shown below.

Table 6

1. 実施例3で得られた粉末	8
2. タルク	2. 8
3. カオリン	1 6
4. マイカ	3
5. 二酸化チタン	1 6
6. ベンガラ	1
7. 黄酸化鉄	3
8. 黒酸化鉄	0. 2
(油相部)	
9. 固形パラフィン	3
10. マイクロクリスタリンワックス	7
11. ワセリン	1 5
12. ジメチルポリシロキサン	3
13. スクワラン	5
14. パルミチン酸イソプロピル	1 7
15. 酸化防止剤	適量
16. 香料	適量

Implementation example 7

Oil base stick foundation

(Powder part)

1. Powder obtained from implementation example 3
2. Talc

3. Kaolin
4. Mica
5. Titanium dioxide
6. bengara
7. iron yellow oxide
8. iron black oxide  
(oil phase part)
9. solid paraffin
10. Microcrystalline wax
11. Vaseline /13
12. Dimethyl polysiloxane
13. squalane
14. palmitic acid isopropyl
15. anti-oxidant suitable amount
16. fragrance suitable amount

[Test method]

9 - 15 is dissolved at 85 deg. C. the powder part is mixed sufficiently in this and added while agitating. Next, it is pulverized and dispersed with a colloidal mixer. 16 is added, after the gas is removed, it is flowed into a container of 70 deg. C and cooled, the foundation of Implementation example 7 is obtained.

In the oil base stick foundation of implementation example 7, the powder obtained in comparison example 3 is

combined instead of the powder obtained from implementation example 3, this is used as comparison example 6.

The implementation example 7 and the comparison example 6 are coated on the skin, the appearance of whiteness right after the coating is checked with the naked eye. The evaluation standard is according to that shown below. The result is shown in Table 7.

Table 7

Implementation example 7	Comparison example 6
○	△

#### Transparency

According to the result of Table 7, the implementation example containing the composite of implementation example 3 does not displayed the whiteness right after application, a beautiful finished foundation can be obtained. The comparison example 6 containing the powder of comparison example 3 shows whiteness during application. Also, the comparison example has difficult coating uniformly. Therefore, similar to the titanium oxide, zinc oxide can improve the dispersion property.

#### Comparison experiment 4

The oil base stick foundation is prepared using the powder obtained in implementation example 4 and the

comparison example 4. Each of the methods is shown in Table 8 and the test methods are given below.

The inventors test the oil base stick foundation using the powder obtained from implementation example 4 and comparison example 4. Then, the comparison is carried out for the cosmetic that used the powder of implementation example 4 of the invention that is compounded with the cerium oxide and silica sol and the cosmetic that used the powder of comparison example 4 that is compounded not using the silica sol. Both of these methods are shown in Table 8, the test methods are shown below

/14

Table 8

1. 実施例4で得られた粉末	8
2. タルク	2. 8
3. カオリン	1 6
4. マイカ	3
5. 二酸化チタン	1 6
6. ベンガラ	1
7. 黄酸化鉄	3
8. 黒酸化鉄	0. 2
(油相部)	
9. 固形パラフィン	3
10. マイクロクリスタリンワックス	7
11. ワセリン	1 5
12. ジメチルポリシロキサン	3
13. スクワラン	5
14. パルミチン酸イソプロピル	1 7
15. 酸化防止剤	適量
16. 香料	適量

Implementation example 8 The oil base stick foundation

(Powder part)

1. Powder obtained from implementation example 4
2. Talc
3. Kaolin
4. Mica
5. titanium dioxide
6. bengara



7. iron yellow oxide
8. iron black oxide
- (oil phase part)
9. solid paraffin
10. Microcrystalline wax
11. Vaseline
12. Dimethyl polysiloxane
13. squalane
14. palmitic acid isopropyl
15. anti-oxidant                      suitable amount
16. fragrance                         suitable amount

[Test method]

9 - 15 is dissolved at 85 deg. C. the powder part is mixed sufficiently in this and added while agitating. Next, it is pulverized and dispersed with a colloidal mixer. 16 is added, after the gas is removed, it is flowed into a container of 70 deg. C and cooled, the foundation of Implementation example 8 is obtained.

In the oil base stick foundation of implementation example 8, the powder obtained in comparison example 4 is combined instead of the powder obtained from implementation example 4, this is used as comparison example 7. /15

The implementation example 8 and the comparison example 7 are coated on the skin, the appearance of

whiteness right after the coating is checked with the naked eye. The evaluation standard is according to that shown below. The result is shown in Table 9.

Table 9

Implementation example 8	Comparison example 7
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○	△
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#### Transparency

According to the result of Table 9, the foundation of implementation example 8 containing the composite of implementation example 4 does not displayed the whiteness right after application, a beautiful finished foundation can be obtained. The comparison example 7 containing the powder of comparison example 4 shows whiteness during application. Also, the comparison example 7 has difficult coating uniformly. Therefore, similar to the titanium oxide, cerium oxide can improve the dispersion property.

The implementation example of the cosmetic combined with the metal oxide/silica composite of the invention is shown in below.

# Implementation example 9

1. タルク	6
2. ステアリン酸処理した実施例1記載の酸化チタン/シリカ複合体	1 2
3. ステアリン酸処理微粒子酸化亜鉛	8
4. オクチルメトキシシンナメート	5
5. 流動パラフィン	1
6. デカメチルシクロペンタシロキサン	2 6. 8
7. ジメチルポリシロキサン	1 6
8. ポリオキシエチレン変性ジメチルポリシロキサン	2
9. イオン交換水	1 5
10. 1, 3-ブチレングリコール	8
11. 防腐剤	0. 1
12. 香料	0. 1

## 2 layer type W/O sun screen

1. Talc
2. Titanium oxide/silica composite of Implementation example 1 that is processed with stearic acid
3. stearic acid processed fine particle zinc oxide
4. octyl methoxy cinnamate
5. fluid paraffin
6. decamethyl cyclo penta siloxane
7. dimethyl polysiloxane
8. polyoxy ethylene modified dimethyl polysiloxane
9. ionic exchanged water

10. 1,3 - butylene glycol

11. Rust proofing agent

12. Fragrance

/16

(The production of the stearic acid processed powder)

5 parts of stearic acid is added to 100 parts of ethanol and dissolved. 20 parts of powder is added and mixed. This dispersed solution is heated above 90 degree while agitating, the solvent is removed, the stearic acid processed powder is obtained.

[Production method]

4 - 8 are heated and mixed at 70 deg C, this is the oil phase. Separately, 10 and 11 are dissolved in 9. This is the water phase. The powder of 1 - 3 is added to the oil phase, it is dispersed in a homogenous mixer. The water phase is added in this. This is emulsified with the homogenous mixer. In addition, 12 is mixed and filled into a container.

Implementation example 10      the solid powder foundation

1. シリコーン処理タルク	11. 4
2. シリコーン処理マイカ	41
3. シリコーン処理二酸化チタン	10
4. シリコーン処理した実施例1記載の酸化チタン/シリカ複合体	10
5. シリコーン処理した実施例3記載の酸化セリウム/シリカ複合体	8
6. シリコーン処理ベンガラ	1
7. シリコーン処理黄酸化鉄	3
8. シリコーン処理黒酸化鉄	0. 2
9. ナイロンパウダー	2
10. ジメチルポリシロキサン	8. 5
11. オクチルメトキシシンナメート	1
12. ポリオキシエチレン変性ジメチルポリシロキサン	0. 6
13. モノオレイン酸ポリオキシエチレンソルピタン	1
14. オクタン酸イソセチル	2
15. エチルパラベン	0. 2
16. 香料	0. 1

1. Silicon processed talc
2. Silicon processed mica
3. Silicon processed titanium dioxide
4. Titanium oxide/silica composite of implementation example 1 that is Silicon processed
5. Titanium oxide/silica composite of implementation example 3 that is Silicon processed
6. Silicon processed bengara
7. Silicon processed yellow iron oxide
8. Silicon processed black iron oxide

9. Nylon powder

10. Dimethyl polysiloxane

11. Octyl methoxy cinnamate

12. polyoxy ethylene modified dimethyl polysiloxane

13. mono-oleic acid polyoxy ethylene sorbitan

14. octane acid isocetyl

15. Ethyl paraben

16. Fragrance

[Production method]

10 - 15 is heated and dissolved (this becomes the oil phase). Separately, 1 - 9 are mixed in a blender. It is mixed in the first oil phase. In addition, 16 is mixed uniformly and sprayed. This is pulverized with a pulverizer. This is compressed and molded. /17

Implementation example 11

The W/O type foundation

1. セリサイト	5
2. カオリン	4
3. 二酸化チタン	6
4. ベンガラ	0. 3 6
5. 黄酸化鉄	0. 8
6. 黒酸化鉄	0. 1 6
7. 実施例 4 記載の酸化亜鉛／シリカ複合体	4
8. 流動パラフィン	5
9. デカメチルシクロペンタシロキサン	2 9
10. ポリオキシエチレン変性ジメチルポリシロキサン	4. 5
11. イオン交換水	3 6
12. 1, 3-ブチレングリコール	5
13. 防錆剤	0. 1
14. 香料	0. 0 8

1. silicite	
2. Kaolin	
3. Titanium dioxide	
4. Bengara	
5. Yellow iron oxide	
6. Black iron oxide	
7. Zinc oxide/silica composite of Implementation example	4
8. Fluid paraffin	
9. Decamethyl cyclo penta siloxane	
10. polyoxy ethylene modified dimethyl polysiloxane	
11. Ionic exchanged water	

12. 1,3 - butylene glycol

13. Rust proof agent

14. Fragrance

[Production method]

8 - 10 is heated to 70 - 80 deg. C and dissolved (this becomes the oil phase). Also, 12 - 13 are dissolved in 11 (this becomes the water phase. 1-7 are mixed, the first oil phase is added to this. This is mixed with a homogenous mixer. After 14 is added and mixed, the water phase is added and emulsified, this is filled into a container.

Implementation example 12 Lipstick

1. 実施例2記載の酸化チタン／シリカ複合体	10
2. 赤色201号	0.6
3. 赤色202号	1
4. 赤色223号	0.2
5. キャンデリラロウ	9
6. 固形パラフィン	8
7. ミツロウ	5
8. カルナバロウ	5
9. ラノリン	11
10. ヒマシ油	23.2
11. 2-エチルヘキサン酸セチル	17
12. イソプロピルミリスチン酸エステル	10
13. 酸化防止剤	適量
14. 香料	適量



1. Titanium oxide/silica composite of implementation

example 2

2. Red color number 201

3. Red color number 202

4. Red color number 223

5. Candiriraro

/18

6. Solid paraffin

7. beeswax

8. Cannavaro

9. Lanolin

10. Castor oil

11. 2-ethyl hexane acid cetyl

12. isopropyl myristyl acid ester

13. antioxidant                      suitable amount

14. Fragrance                      suitable amount

[Production method]

1 - 3 are mixed with a part of 10. The roller is processed (this has become a dye part). 4 is dissolved in a part of 10 (this is the stain material part). 5 - 13 are mixed. After the heating and dissolving are performed, the dye part and the staining part are added and dispersed uniformly in a homogenous mixer. This is flowed rapidly into a mold, a stick is formed.

Implementation example 13

1. タルク	3. 0
2. 実施例 5 の酸化チタン／シリカ／アルミナ複合体	12. 0
3. ベントナイト	0. 5
4. モノステアリン酸ポリオキシエチレンソルビタン	0. 9
5. トリエタノールアミン	1. 0
6. プロピレングリコール	10. 0
7. イオン交換水	51. 1
8. ステアリン酸	2. 2
9. イソヘキサデシルアルコール	7. 0
10. モノステアリン酸グリセリン	2. 0
11. 液状ラノリン	2. 0
12. 流動パラフィン	8. 0
13. 防腐剤	0. 2
14. 香料	0. 1

O/W type sun screen (liquid type)

1. Talc
2. Titanium oxide/silica/alumina composite of  
implementation example 5
3. Bentonite
4. Monostearic acid polyoxy ethylene sorbitan
5. Triethanol amine
6. Propylene glycol
7. Ionic exchanged water
8. Stearic acid
9. Isohexa decal alcohol

10. Monostearic acid glycerin

11.liquid lanolin

12.liquid paraffin

13.rust proofing agent

14.Fragrance

/19

[Production method]

3 is dispersed into 6. This is added to 7, the temperature is raised to 70 deg C, and mixed in a homogenous mixer. In addition, 4 and 5 are added to this and this becomes the water phase. Also, 8 - 13 are added and heated to 70 - 80 deg C, this becomes the oil phase. 1 and 2 are added to the water phase and agitated. It is processed at 70 deg C and processed with a homogenous mixer. 14 is mixed in and then cooled and filled into the container.

According to the invention, the metal oxide particle of primary particle size of 1 - 1000 nm consists of the metal oxide/silica composite in the silica particle at the primary particle form, the dispersion of the metal oxide is improved. The cosmetic that is obtained has sufficient particle size to provide a good UV ray protection capability.

/20

#### Scope of Patent claims

1.The metal oxide/silica composite of the invention is characterized as a finely dispersed system comprising metal oxide particles having a primary particle diameter of 1 to 1000 nm.

2.The metal oxide/ silica composite of the invention of Claim 1 is characterized with (1) the dispersion body containing a silica sol of primary particle size of 1 - 150 nm and (2) a particular metal oxide or metal oxide sol having a primary particle diameter of 1 to 1000 nm.

3.The metal oxide/silica composite of the invention of Claim 1 or 2, after mixing the aforementioned dispersion body and the metal oxide of fine particles or the metal oxide sol, the pH of the solution is changed, the silica and metal oxide are coagulated and precipitated simultaneously.

4.. The metal oxide/silica composite of the invention of Claim 1 or 2, wherein the particulate metal oxide or metal oxide sol comprises one or more of titanium oxide, zinc oxide and cerium oxide, 1 or more than 2 of these can be combined.

5.The metal oxide/silica composite of the invention of Claim 1 - 4 is characterized as the metal oxide/silica composite of gel composition.

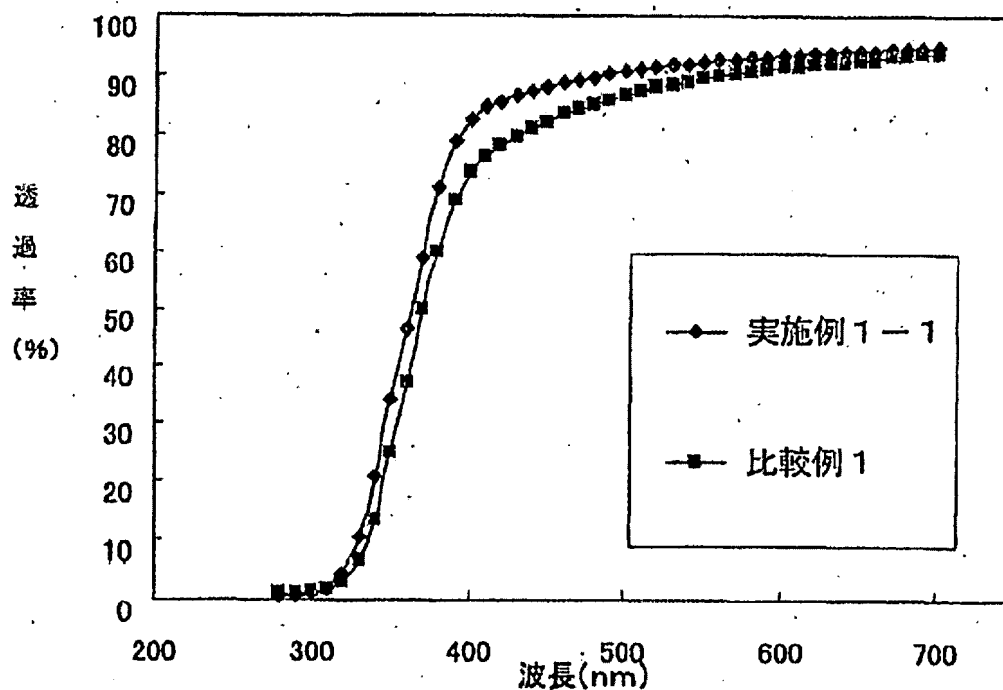
6. The metal oxide/silica composite of the invention of Claim 5 is characterized as the powder composition obtained by drying the aforementioned gel composition.

7. It is preferred that the composite amount of the metal oxide is 5 - 90 wt. % to the total composite in the metal oxide/silica composite of the invention of Claim 1 - 6.

8. The cosmetic of the invention of Claim 1 - 7 is characterized as combining the aforementioned metal oxide/silica composite.

DIAGRAM

Figure 1



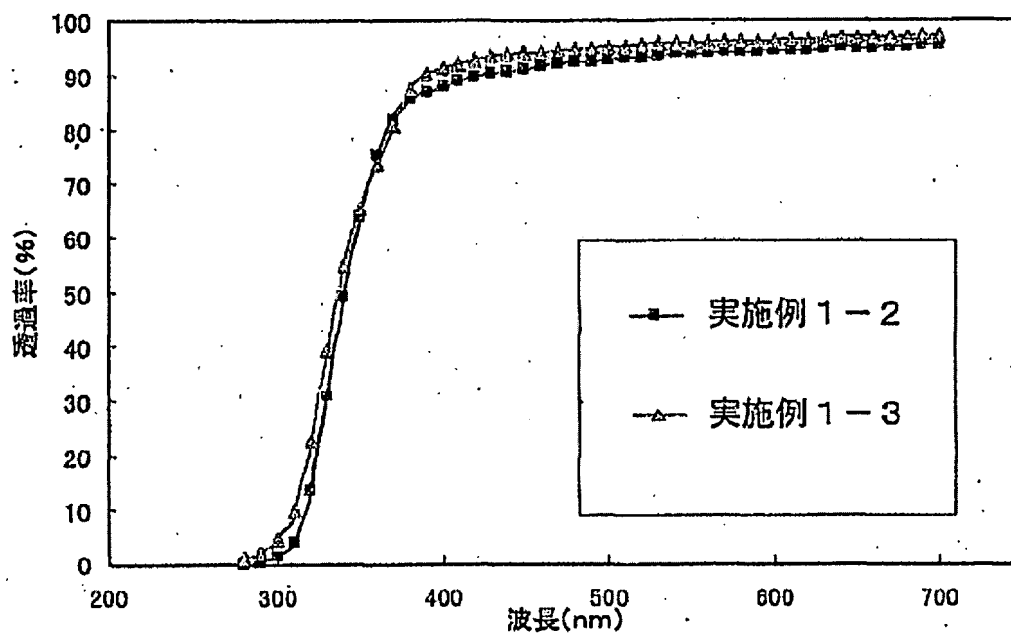
Permeability (%)

Wavelength (nm)

Implementation example 1 - 1

Comparison example 1

Figure 2



Permeability (%)

Wavelength (nm)

Implementation example 1 - 2

Implementation example 1 - 3

Figure 3

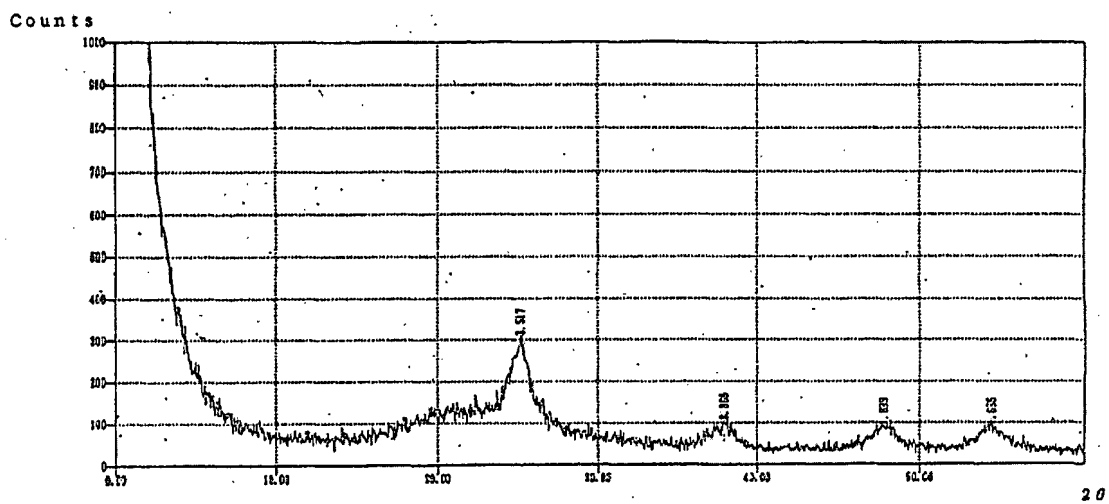
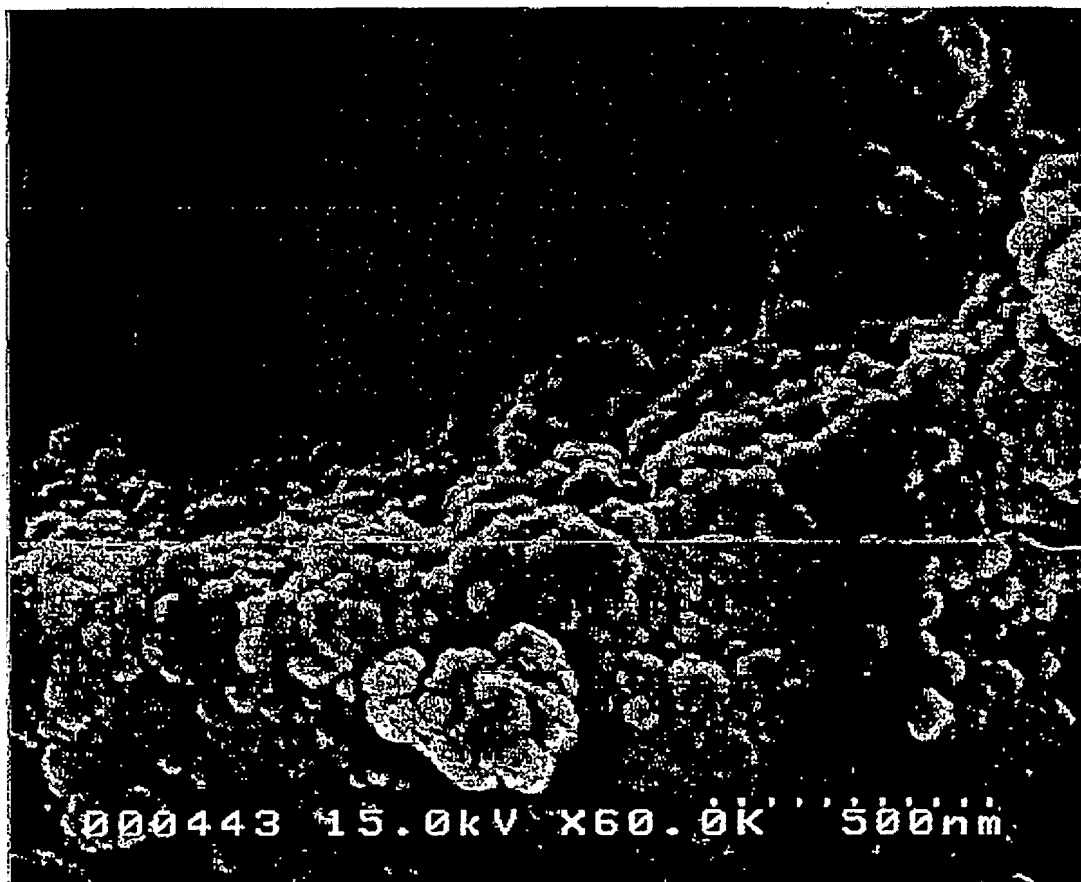


Figure 4



0 500nm

Figure 5



